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(54) **Methyl-esterification of deodorisation distillates of oils**

(57) A method of methyl-esterification of free fatty acids in deodorisation distillates of oils by reaction with methanol comprises contacting the reactants with a cation-exchange resin in a fluidised state.

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SPECIFICATION

Method of methyl-esterification of deodorisation distillates of oils

5 The present invention relates to a method of methyl-esterification of free fatty acids in the deodorisation distillates which are formed as by-products in the deodorisation step of a process for purifying fats and fatty oils (referred to herein as "oils").

10 In a conventional purification process, oils such as soybean, rape-seed, cotton seed, safflower, sunflower, rice-bran, corn, coconut, palm and palm kernel oil are treated in a number of steps, one of which is deodorisation. In deodorisation, scum, slag, hotwell oil foots and other by-products (referred to herein as "deodorisation distillates" or merely "distillates") are formed, and which include, for instance, tocopherols, sterols, hydrocarbons, glycerides and/or free fatty acids.

15 Free fatty acids may comprise from 30 to 70, and tocopherols from 0.5 to 20, % by weight of the total of the distillates. The tocopherols can have utility as drugs, foods or anti-oxidants. It has generally been necessary to separate free fatty acids from the distillates before the desired tocopherols can be condensed out. Conventionally, free fatty acids have been separated by methyl-esterification and subsequent recovery by, for example, molecular distillation or ion-exchange. Other separation methods involve solvent fractionation of the distillates, often after hydrogenation, or vacuum distillation of the distillates.

20 For instance, free fatty acids have conventionally been esterified by mixing one volume of the deodorisation distillates, if desired after saponification, with from 1 to 10 volumes of methanol, adding an acidic or basic catalyst, to cause esterification, and separating the residual catalyst by neutralisation or washing. The product of methyl-esterification is then used in producing tocopherol condensates by vacuum distillation, molecular distillation or ion-exchange, as described above.

25 The solubility of the distillates in methanol is low. It is therefore necessary, in the conventional esterification process described above, that non-polar solvents such as toluene and hexane are added, or that the mixture is stirred to maintain the heterogeneous reaction. Undesirably complicated apparatus is therefore necessary.

30 Further, separation of residual catalyst by neutralisation requires subsequent, difficult separation of the resultant salt. Separation of the residual catalyst by washing, with water, provides conditions in which the deodorisation distillate can easily emulsify, owing to the presence of sterols remaining after sterol isolation. These factors make it difficult to isolate the methyl-esterification products.

35 According to the present invention, a

method of methyl-esterification of deodorisation distillates of oils, by reaction with methanol, is conducted in the presence of a cation-exchange resin in a fluidised state.

40 The method of the present invention avoids the need for solvent or acid or base catalyst. In particular, it has been found that potential alternative procedures for esterification involving ion-exchange, by shaking or using a fixed bed, are generally unsatisfactory. Shaking causes the disadvantageous adhesion of methanol-insoluble ingredients of the distillates to the ion-exchange resin, unless a large quantity of methanol is used as a washing aid, during reaction or in regeneration. If a fixed bed is used, the reaction is essentially heterogeneous, and methanol-insoluble constituents precipitate out unless a non-polar solvent is added. The method of the present invention means that there is reduced adhesion and avoidance of the need for a further solvent while allowing satisfactory esterification continuously and efficiently. The final acid values of deodorisation distillates treated by the method of the invention are apparently considerably less than when other ion-exchange methods are used, an indication of high efficiency.

45 The method of the invention may be conducted in what is effectively a fluidised bed. The ion-exchange resin is packed in a column, a mixture of the distillates and methanol is passed upwardly through the column at a flow rate sufficient to maintain the resin in a fluidised state, and methyl-esterification products are collected from the top of the column. Various conventional ion-exchanges methods, such as the counter-contact, McIlheny and McConnel, McNeil, Swinton & Weisc, and SRI methods, may be used in the method of the present invention.

50 The cation-exchange resin may be in the form of particles of any reasonable size. Various functional groups may be used but strongly acidic functional groups, e.g. a sulphonic group, are preferred. Hydrogen-type ion-exchange resins are particularly preferred in order that there are no potentially interfering cations. The commercially-available cation-exchange resins DIA ION PK206 and DIA ION PK208, manufactured by Mitsubishi Chemical Industries Ltd., are particularly suitable.

55 The methanol:distillates ratio is 1:1 to 1:50, and preferably 1:2 to 1:10. The reaction may be conducted at any temperature no greater than the boiling point of methanol, and preferably at from 50-65 C. The upward flow rate through a column containing the resin is preferably from 0.32 to 2.5 m/min. Regeneration may be unnecessary.

60 The following Examples illustrate the invention, in comparison with the Comparative Examples. The given acid values were determined in each case by the standard method of the Japan Oil Chemist's Society after extract-

ing methanol in the solution by distillation.

Comparative Examples 1 and 2 and Example 1

- 5 Methyl-esterifications were practised at a liquid temperature of 60 C, respectively by the shaking method, the downward-flow method and the fluidisation method, using a solution prepared by mixing, and fully dispersing, 1 volume of deodorisation distillates of soybean oil (acid value = 76.8) with 2 volumes of methanol, and the cation-exchange resin DIA ION PK206, converted into the hydrogen form in the usual manner.
- 10 The shaking method was carried out by placing the cation-exchange resin in a Sakaguchi flask, adding the solution until the liquid surface reached to the upper surface of the resin, and reacting in a thermostat with shaking apparatus. The precipitates formed during the reaction were washed with methanol and mixed with the solution. After 1, 2 and 4 hours, the acid values were 7.2, 4.8 and 4.3, respectively.
- 15 The downward-flow method was carried out by filling a hot column provided with a jacket, and reacting the solution using a flow rate having a specific velocity of 1 or 2. The respective acid values were 3.9 and 5.7; the oily substance precipitating in the column was discounted in measuring the acid values.
- 20 The fluidisation method was carried out by filling a hot column provided with a jacket, and forming a fluidised bed at a flow rate of 0.5 or 2.0 m/min., and contacting the solution and resin for 2 hours. The respective acid values were relatively low, 0.3 and 1.2.

Example 2

- 40 A solution prepared by mixing, and fully dispersing, 1 volume of deodorisation distillates of rape-seed oil (acid value = 56.8) with 5 volumes of methanol was passed upwardly through a fluidised column of the cation-exchange resin DIA ION PK208, converted into the hydrogen form in the usual manner. The liquid temperature was 65 C.
- 45 At flow rates of 0.35, 0.5, 1.2 and 2.0 m/min, the respective acid values were 0.3, 0.5, 0.4 and 1.4. Other rates were tested: at a flow rate of 0.25 m/min, no fluidised bed was formed; at a flow rate of 2.5 m/min, the deodorisation distillates overflowed from the top of the column before the methyl-esterification was complete, and these two experiments are effectively outside the scope of the invention.

Example 3

- 60 The procedure of Example 2 was followed, except that the deodorisation distillates of cotton-seed oil (acid value = 68.4) were used. The final acid values at the flow rates of 0.35, 0.5, 1.5 and 2.0 m/min, were 0.4, 0.3, 0.7 and 1.5, respectively.

Examples 4 to 6

- The procedure of Example 2 was followed, except that sunflower oil (acid value = 71.3), safflower oil (acid value = 65.3) and perm oil (acid value = 95.2) were used in these three Examples. In Example 4, at a flow rate of 0.5 m/min, the final acid value was 0.4. In Example 5, at flow rates of 0.5 and 1.5 m/min, the final acid values were 0.3 and 0.8, respectively. In Example 6, at flow rates of 0.5 and 1.5 m/min, the final acid values were 0.5 and 1.0, respectively.

80 CLAIMS

1. A method of methyl-esterification of deodorisation distillates of oils by reaction with methanol, which comprises contacting the reactants with a cation-exchange resin in a fluidised state.
2. A method according to claim 1, which comprises passing the reactants through a fluidised bed at a flow rate of from 0.32 to 2.15 m/min.
3. A method according to claim 1, substantially as described in any of the Examples.

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